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Methods of Soil Analysis for Soil-Fertility Investigations

By

MICHAEL PEECH, Professor of Soil Science
New York Agricultural Experiment Station

L. T. ALEXANDER, Principal Soil Scientist

and

L. A. DEAN, Senior Soil Scientist
Division of Soils, Fertilizers, and Irrigation
Bureau of Plant Industry, Soils, and Agricultural Engineering
Agricultural Research Administration

and

J. FIELDING REED, Research Professor of Agronomy
North Carolina Agricultural Experiment Station

UNITED STATES DEPARTMENT OF AGRICULTURE

In Cooperation With the
New York and North Carolina Agricultural Experiment Stations

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FOREWORD

The methods discussed in this circular, first issued as a mimeographed report by this Bureau in March 1945, are the result of a cooperative study of the nutrient status of soils in the commercial potato-producing areas of the Atlantic and Gulf coasts. The study is one of the few in which a number of State agricultural experiment stations and this Bureau have attempted to develop a standardized set of analytical methods as a part of their soil-fertility investigations. This standardization has enabled workers in one State to compare their work directly with the work done in other States confronted with the same problem.

The active interest in the standardization of methods for soil analysis prompted us to publish this report. By doing this we hope to encourage workers in other regions to standardize the laboratory phases of their soil-fertility investigations.

The committee that prepared this report was generously aided by a large group of other workers who volunteered helpful suggestions. The committee and I wish to express our indebtedness to this group of scientists and the hope that in future an even larger group will have suggestions regarding methods of soil analysis for soil-fertility investigations.

F. W. Parker,
Assistant Chief of Bureau,
In Charge of Soils.

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April 1947 • Washington, D. C.

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By MICHAEL PEECH, *professor of soil science, New York (Ithaca) Agricultural Experiment Station, chairman,* L. T. ALEXANDER, *principal soil scientist,* and L. A. DEAN, *senior soil scientist, Division of Soils, Fertilizers, and Irrigation, Bureau of Plant Industry, Soils, and Agricultural Engineering, Agricultural Research Administration,* and J. FIELDING REED, *research professor of agronomy, North Carolina Agricultural Experiment Station*[1]

United States Department of Agriculture, Bureau of Plant Industry, Soils, and Agricultural Engineering, in cooperation with the New York and North Carolina Agricultural Experiment Stations

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[1] Constituting a committee on methods of soil analysis, informally organized in 1944 by F. W. Parker, assistant chief, Bureau of Plant Industry, Soils, and Agricultural Engineering, Plant Industry Station, Beltsville, Md.

NEED FOR A UNIFORM SET OF LABORATORY METHODS

A COOPERATIVE investigation of the soils used in the commercial production of potatoes was initiated in 1944 by the Alabama, Maine, Maryland, New Jersey, New York, and North Carolina Agricultural Experiment Stations, the Virginia Truck Experiment Station, and the Division of Soils, Fertilizers, and Irrigation of the Bureau of Plant Industry, Soils, and Agricultural Engineering (*3*, *6*, *10*).[2] Within each State a large number of soil samples were collected from potato fields in selected areas. In order that the chemical analytical work in one State might be directly comparable with that of another, it became necessary to agree on a uniform set of laboratory methods. A committee composed of the writers proposed the methods for determining readily soluble phosphorus, pH value, organic matter, exchange capacity, and the exchangeable cations. Their report was approved by the cooperators and constitutes this publication. It is hoped that it will contribute materially toward the much-needed standardization of chemical methods for the examination of soils in similar future soil-fertility investigations.

Needless to say, the adoption of uniform laboratory methods would greatly enhance the value of the analytical work done in the different States. For example, because of the wide variety of chemical methods of soil analysis now in use, it is seldom that two laboratories obtain the same numerical values when determining such an empirical thing as the "available" phosphorus. It is true that each laboratory may be able to arrive at similar conclusions regarding the relative phosphorus status of different soils, but under uniform methods it should be possible for soil investigators in the different States to compare directly their findings with those of others. Although tradition and the wide experience accumulated with a given method frequently dictate one's preference for that particular method, it is hoped that the advantages derived from adopting uniform methods will overshadow many of the disadvantages arising from making such a change.

It might be well to inject a word of caution concerning the general applicability of the methods given in this report. They were considered to give satisfactory indices of soil fertility when applied to the acid, highly fertilized soils of the Atlantic and Gulf Coast States. If applied to calcareous or alkaline soils, however, many of the methods would undoubtedly be less fully satisfactory.

PREPARATION OF SOIL SAMPLES

As soon as possible after sampling, spread the soil sample on a clean sheet of paper and allow it to dry thoroughly. When the aggregates are air-dry, crush them with a rubber-tipped pestle in a mortar without grinding the primary particles. If the sample is large, first crush the large aggregates by rolling with a hardwood rolling pin and then take a subsample by the process of quartering. In either case, crush the aggregates and sift the sample through a sieve with holes 2 mm. in

[2] Italic numbers in parentheses refer to Literature Cited, p. 24.

diameter. Return the coarse material retained on the sieve to the mortar for further crushing, taking due precautions not to grind any primary particles.

In some soils it is rather difficult to discriminate between the weathered rock and the soil; here the operator must use his own judgment. Pick out and set aside any gravel, iron concretions, or rocks that may be present and combine later with the material that does not pass through the 2-mm. sieve. Repeat this process of crushing and sieving until only the primary particles and organic residues remain on the sieve. This coarse material may be discarded.

Mix well the soil material passing the 2-mm. sieve and store in an airtight container. This constitutes the stock sample on which all the determinations here described are made.

DETERMINATION OF READILY SOLUBLE PHOSPHORUS BY THE MODIFIED TRUOG METHOD

Reagents

Extracting solution, pH 3.—Dilute standard stock 0.1 N sulfuric acid solution to 0.002 N and add 3 gm. of ammonium sulfate per liter.

Molybdenum blue reagent.—Place 19.5 gm. of MoO_3 (99.5–100 percent) in 800-ml. Kjeldahl flask, add 500 ml. of concentrated sulfuric acid (36 N), and heat with gentle mixing until solution is complete. Cool to 150° C. Weigh, on a small watch glass, 1.25 gm. of molybdenum metal powder (200 mesh, 99.5–100 percent) and transfer to the Kjeldahl flask. Keep at a temperature of 140°–150° C., taking precautions not to exceed 150° C., and mix vigorously until the molybdenum metal is dissolved. The few large particles that do not readily dissolve may remain. Cool, dilute a 5-ml. aliquot of this reagent with 20 ml. of water, and titrate with 0.1 N $KMnO_4$ to a pink that persists for a minute. The reagent should be 0.11 N; if less than 0.109 N, add a calculated quantity of molybdenum and dissolve by reheating in a Kjeldahl flask to 150° C. When stored in the dark in a Pyrex glass-stoppered bottle, the reagent will keep indefinitely.

Dilute molybdenum blue reagent.—Dilute 1 volume of the above molybdenum blue reagent with 3 volumes of water, and cool. This dilute reagent deteriorates upon standing and should be freshly prepared as needed.

Sodium bisulfite solution, 8 percent.—Dissolve 40 gm. of sodium bisulfite (meta, powder) in 500 ml. of 1.0 N sulfuric acid. Prepare a fresh supply every week.

Standard stock phosphate solution, 50 γ of P per milliliter.—Dissolve 0.2195 gm. of pure dry KH_2PO_4 in water, add 25 ml. of 1 N sulfuric acid, and dilute with water to 1 liter.

Calibration curve

Dilute 100 ml. of the standard stock phosphate solution with water to 500 ml. (1 ml.=10 γ P). Measure out aliquots of this solution, containing 0 to 150 γ of P, into a series of 50-ml. volumetric flasks, dilute to 35 ml. with water, add 4 ml. of sodium bisulfite solution, and proceed with color development as directed under the procedure. Plot the transmittancies of the standards against the micrograms of phosphorus taken on semilogarithmic graph paper.

Procedure

Place 4 gm. of soil in a shaking bottle, add 400 ml. of the extracting solution, stopper, and shake for 30 minutes in a reciprocating or end-over-end shaker. Filter through 11 cm. Whatman No. 42 filter paper, discarding the filtrate until it comes through perfectly clear. Transfer a 35-ml. aliquot of the filtrate to a 50-ml. volumetric flask, add 4 ml. of sodium bisulfite solution, and place the flasks in a boiling-water bath for 40 minutes. Then, using a 10-ml. measuring pipette, add 2 ml. of the dilute molybdenum reagent, directing the stream into the solution (do not allow it to run down the side of the flask), mix immediately by swirling, and continue to heat in the boiling-water bath for exactly 25 minutes. Cool rapidly in cold water, dilute to volume with water, and mix. Measure the transmittancy at 650 mμ (use a red filter). The color is stable for as long as 24 hours. If the color is too intense, the determination should be repeated. Place a smaller aliquot in a 50-ml. volumetric flask, dilute to 35 ml. with water, and proceed with the color development as directed above.

For a 35-ml. aliquot, micrograms of P found × 13 = pounds of P_2O_5 per 2,000,000 pounds of soil.

Comments

A method employing the Truog (*14*) extracting solution was selected for the determination of readily soluble phosphorus. In proposing this method, however, it is realized that all chemical methods for the determination of readily soluble phosphorus in soils are quite empirical and that other chemical methods now in use are capable of giving equally satisfactory evaluation of the phosphorus status of different soils when properly correlated against known crop responses to phosphorus fertilization. Also data comparing some of the common methods of determining readily soluble phosphorus on the highly fertilized acid soils common to the potato areas of the East indicated that one chemical method of evaluation will probably give as much relative information as another (*12*).

It will be noted that the modified Truog method herein described is a considerable departure from that originally given by Truog. The quantity of phosphorus in the extract is determined by the Zinzadze molybdenum blue reagent as modified by Gerritz (*5*). The reagent as well as the color developed is very stable, and the method is therefore well adapted to present spectrophotometric methods. Provision also is made to prevent the interference of ferric and arsenate ions. The method is not quite so sensitive as that of Truog (*14*), which utilizes stannous chloride as the reducing agent. For this reason, the 1:100 soil-extracting solution ratio was adopted. This procedure extracts somewhat less phosphorus per unit weight of soil than the original Truog method using a 1:200 dilution; however, the relative values for readily soluble phosphorus obtained at 1:100 dilution on different soils are in no way impaired.

The time of shaking during extraction is, of course, arbitrary; with most soils the equilibrium between the soil and the extracting solution is seldom established within the 30-minute period of shaking specified in the procedure. Most consistent results are obtained when the time of contact between the soil and the extracting solution is eliminated

as a variable. For this reason, the shaking should be begun immediately after adding the extracting solution to the soil; likewise after shaking, the suspensions should be filtered as soon as possible. It is not necessary to collect more than 75 ml. of the clear filtrate.

It is important that the standards and unknowns be heated for the same length of time and at the same temperature. The water in the bath should be above the level of the solution in the flasks. Boiling water should be added to the bath from time to time to compensate for evaporation. The use of a water bath made of sheet copper, provided with a ½-inch mesh wire screen to hold 24 flasks about an inch from the bottom, is very convenient for both heating and cooling the flasks.

Unfortunately this method of color development is not sufficiently sensitive for use on soils containing less than 50 pounds of P_2O_5 per 2,000,000 pounds of soil. When dealing with such soils the method of Truog (*14*), utilizing stannous chloride for reduction, may be preferable. In applying Truog's stannous chloride method for use with a photoelectric colorimeter, the time of color development and the quantity of stannous chloride added must be carefully standardized.

DETERMINATION OF pH

Procedure

To a 20-gm. sample of soil in a 50-ml. beaker, add 20 ml. of distilled water and stir the suspension several times at regular intervals for about an hour. Measure the pH of the soil suspension with the glass electrode, stirring well just prior to immersing the electrodes deep into the suspension.

Comments

Soil-water ratios ranging from 1:0.5 to 1:10 have been proposed for the determination of the pH of soils. The pH of most soils increases with dilution, usually attaining approximately a constant value at 1:5 soil-water ratio. There is little justification for using soil-water ratios wider than 1:1. The pH measurements of soils at moisture contents below that of the moisture equivalent are subject to several inherent errors, as recently pointed out by Davis (*4*), and also make mandatory the use of a special glass electrode and pH meter.

DETERMINATION OF ORGANIC MATTER

Reagents

1 N potassium dichromate.—Dissolve 49.04 gm. of reagent grade $K_2Cr_2O_7$ in water and dilute to 1 liter.

0.5 N ferrous sulfate.—Dissolve 140 gm. of reagent grade $FeSO_4.7H_2O$ in water, add 40 ml. concentrated H_2SO_4, cool, and dilute to 1 liter. Standardize this reagent each day by titrating against 10 ml. of N potassium dichromate, as directed in the method given below.

Barium diphenylaminesulfonate.—Prepare a 0.16 percent aqueous solution.

o-phenanthroline ferrous complex (optional).—Prepare 0.025 M solution of one of the phenanthroline ferrous complex indicators.

Sulfuric acid; not less than 96 percent.

Phosphoric acid; 85 percent, U. S. P. grade.

Procedure

Transfer a weighed quantity of soil (ground to pass a 0.5-mm. sieve) containing 10 to 25 mg. of organic carbon into a 500-ml. Erlenmeyer flask, and add 10 ml. of N potassium dichromate. Then add rapidly 20 ml. of concentrated sulfuric acid, directing the stream into the solution. Immediately swirl vigorously by hand for 1 minute and let the flask stand on a sheet of asbestos for about 30 minutes. Then add 200 ml. of water, 10 ml. of phosphoric acid, and 0.5 ml. of barium diphenylaminesulfonate indicator.

Proceed with the titration as follows: Add the ferrous sulfate solution until the solution is purple or blue, then add the ferrous sulfate in small lots of about 0.5 ml. until the color flashes to green with little or no warning. Add 0.5 ml. of N potassium dichromate to restore an excess of dichromate and complete the titration by adding ferrous sulfate drop by drop to a light-green end point. If more than 8 ml. of the available 10 ml. of potassium dichromate is reduced, the determination should be repeated with less soil.

Percentage of organic matter in soil sample=

$$\frac{(\text{Milliliters of 1 N } K_2Cr_2O_7 \text{ reduced}) \times 0.69}{\text{Weight of sample (gm.)}}$$

Comments

The estimation of soil organic matter based on the use of the conventional empirical factor for converting organic carbon to organic matter may be subject to considerable error even when the organic carbon is determined accurately by the more tedious dry-combustion method. For this reason the more rapid chromic acid-titration methods are now widely used. The proposed method for the determination of organic carbon is a slight modification of the method described by Walkley (*15*). Despite its simplicity it has been shown to give results that agree closely with those obtained by the dry-combustion method when applied to a wide variety of soils.

In this method the soil is digested with a mixture of chromic and sulfuric acids, making use of the heat of dilution of sulfuric acid. Consequently, it is necessary to add the sulfuric acid rapidly and to cool the flasks uniformly on a sheet of asbestos. The unpublished results of Peech indicate that the volume of the dichromate solution and the concentrated sulfuric acid may be reduced to half that specified in the procedure without significantly affecting the results, provided, of course, that the size of the soil sample is also proportionately reduced.

The color change of the optional *o*-phenanthroline indicator occurs at a much higher oxidation-reduction potential, and this indicator is theoretically superior to diphenylamine. With certain soils, however, the color change of diphenylamine is more easily observed than that of *o*-phenanthroline; hence, both indicators are recommended. The aqueous solution of barium diphenylaminesulfonate indicator is much more stable than that prepared by dissolving diphenylamine in concentrated sulfuric acid.

Nitrates interfere only if present in quantities in excess of one-twentieth of the carbon content. Carbonates, even when they constitute 50 percent of the soil, do not affect the results. Elemental carbon,

as charcoal or coal, is practically unattacked in this method, so this source of error is eliminated. Interference due to significant quantities of chlorides can be overcome by the addition of silver sulfate to the sulfuric acid, or a correction can be applied if the quantity of chlorides is known. When chlorides are present in quantities less than the molecular equivalent of carbon, 1.25 gm. of silver sulfate should be dissolved in each 100 ml. of concentrated sulfuric acid.

DETERMINATION OF EXCHANGEABLE CATIONS AND EXCHANGE CAPACITY

The exchangeable metal cations are determined after extraction of the soil with 1 N ammonium acetate solution. The advantages of this reagent have been pointed out by Schollenberger and Simon (*13*). Specific procedures for the determination of the exchangeable cations and the cation exchange capacity using this reagent have been described by Schollenberger and Simon (*13*) and Peech (*8*, *9*). Tentative procedures for the determination of the exchangeable cations and the exchange capacity, also based on the use of 1 N ammonium acetate as the replacing salt solution, are listed in Methods of Analysis of the Association of Official Agricultural Chemists (*1*, *p. 13*).

Several investigators, however, have questioned the general applicability of the ammonium acetate method for the determination of the exchangeable hydrogen and the exchange capacity. Admittedly, all current methods for the determination of the exchangeable hydrogen and the exchange capacity are quite empirical, involving many different definitions of these concepts and rigid adherence to well-defined procedures.

The objection that has been raised to the ammonium acetate method for the determination of exchangeable hydrogen is that it gives low values for the 1 : 1 type clays and for the organic soils. Consequently, the exchange capacity for the 1 : 1 type clays and for organic soils is also low, owing to incomplete replacement of the exchangeable hydrogen. On the other hand, the ammonium acetate method gives results for the exchange capacity and the exchangeable hydrogen (by difference) on many mineral soils containing the 2 : 1 type clays that are consistent and in close agreement with Bradfield's (*2*) definition of a fully saturated soil in the presence of excess $CaCO_3$ in equilibrium with the partial pressure of the CO_2 in the atmosphere. For this reason, a direct method is also suggested for exchangeable hydrogen, utilizing a modification of Mehlich's triethanolamine procedure (*7*).

It is hoped that sufficent data for exchangeable hydrogen will be obtained, using both the ammonium acetate and the triethanolamine methods, to permit more definite conclusions regarding the relative merits of these two procedures.

Specific detailed macro- as well as micro-procedures are outlined for the determination of the exchangeable metal cations in the ammonium acetate extracts. The micromethods herein described are essentially those previously reported by Peech (*9*). It will be noted that the same quantity of soil is taken for extraction regardless of whether the macro- or the micromethods are to be employed, even

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though a smaller sample was recommended by Peech (*9*) for the micromethods. It was thought that the extraction should be thoroughly standardized in order that the results obtained by different laboratories may be comparable. If it can be shown that reducing the weight of the sample in proportion to the volume of the ammonium acetate solution does not affect the results of determination of any of the exchangeable cations, then the size of the sample can be reduced to great advantage when using the micromethods, with considerable saving of time and reagents. Pending further work, however, it is suggested that all collaborators follow exactly the same extraction procedure herein outlined.

Extraction and Preparation of Solution for Analysis

Reagent

Ammonium acetate, 1 N, pH 7.0.—Prepare a sufficient volume, preferably in a Pyrex bottle, by mixing 70 ml. of ammonium hydroxide, specific gravity 0.90, and 58 ml. of 99.5 percent acetic acid per liter of solution desired. After cooling, adjust exactly to pH 7.0 and dilute to volume with water.

Procedure

Weigh out 50 gm. of air-dry 2-mm. soil into a 250-ml. Erlenmeyer flask and add 100 ml. of ammonium acetate solution. Stopper, shake the flask for several minutes, and allow to stand overnight. Transfer the contents of the flask to a small Buchner funnel (Coors No. 1) fitted with moist 5.5-cm. Whatman No. 42 filter paper and filter, applying gentle suction. Leach the soil with an additional 400 ml. of ammonium acetate, adding small portions of ammonium acetate at a time and using gentle suction, so that the leaching process will require not less than 1 hour.

Transfer the filtrate to a 600-ml. Pyrex beaker and evaporate to complete dryness. Cool, cover the beaker with a watch glass, and add slowly through the lip 10 ml. of concentrated nitric acid (preferably fuming) and 2 ml. of concentrated hydrochloric acid. Warm until the reaction has subsided and the brown fumes are no longer given off. Rinse the watch glass into the beaker, transfer the solution to a 150-ml. Pyrex beaker, and evaporate to dryness at low heat to prevent spattering.

Continue to heat for about 10 minutes to dehydrate the salts; then place the beaker in an electric muffle at about 150° C., heat to 390° ± 10°, and hold at this temperature for about 20 minutes. Remove the beaker from the muffle and cool. Treat the residue with 3 ml. of 6 N hydrochloric acid, evaporate to dryness at low heat, and continue heating for about 30 minutes longer to dehydrate silica. Cool and dissolve the residue in 0.1 N HNO_3, using a rubber policeman to loosen the residue of salts; transfer to a 100-ml. volumetric flask, make to volume with 0.1 N HNO_3, and mix well.

If the micromethods as outlined on page 16 are to be followed, transfer to a 25-ml. volumetric flask and make to volume with 0.1 N HNO_3. In either case filter off the silica or allow it to settle out and take aliquots of the clear supernatant liquid. Designate this as *Solution A*.

Comments

The excess of ammonium acetate should be expelled by evaporation to complete dryness before the addition of nitric acid; otherwise the violent decomposition of the large quantity of ammonium nitrate upon subsequent heating may result in some loss of the residue of salts by puffing out of the beakers. As shown by Peech (*8*) this simple procedure effects complete removal of the ammonium salts and organic matter without any loss of alkalis by volatilization.

Occasionally when dealing with soils extremely low in exchangeable metal cations (acid sandy soils), some carbon may be formed during the ignition. This carbon resists further ashing at 390° C., even upon repeated evaporation with nitric acid and ignition, but may be partly destroyed by evaporation with 1 ml. of 30 percent hydrogen peroxide. With soils high in exchangeable manganese, the residue from the ignition will be dark, owing to manganic oxide, which should not be mistaken for carbon.

Determination of the Cation Exchange Capacity

Direct distillation of adsorbed ammonia

(Recommended for calcareous soils only)

Reagents

95 percent ethyl alcohol, U. S. P.—Test for acidity as follows: Mix 50 ml. of alcohol with 35 ml. of CO_2-free water, add a few drops of phenolphthalein, and titrate with 0.05 N NaOH to a slight pink color. Not more than 0.2 ml. of the NaOH should be required.

Sodium chloride, U. S. P. grade.

Antifoam mixture.—Mix equal parts of mineral oil and capryl alcohol.

1 N NaOH; standard 0.2 N H_2SO_4; and standard 0.1 N NaOH.

Procedure

Wash out the excess of ammonium acetate from the ammonium-saturated soil on the Buchner funnel remaining after the extraction of the exchangeable cations with 200 ml. of 95 percent ethyl alcohol, using small portions of alcohol at a time and draining well between each addition. Transfer the soil with the filter paper to a Kjeldahl flask, add 400 ml. of water, about 10 gm. of NaCl, 5 drops of antifoam mixture, and 25 ml. of 1 N NaOH. Connect the flask with the condenser and distill 200 ml. into 60 ml. of standard 0.2 N H_2SO_4. Titrate the excess of acid with standard 0.1 N NaOH, using methyl red as the indicator.

Distillation of adsorbed ammonia after extraction with sodium chloride

Reagents

Acidified sodium chloride solution, 10 percent.—Prepare an aqueous 10 percent solution of NaCl, U. S. P. grade (ammonia-free), and acidify with HCl to render the solution approximately 0.005 N with respect to acidity.

1 N NaOH; standard 0.2 N H_2SO_4; and standard 0.1 N NaOH.

Procedure

After washing the soil with alcohol to remove the excess of ammonium acetate as directed in determining adsorbed ammonium by direct distillation, extract the adsorbed ammonium by leaching the soil with 450 ml. of acidified 10 percent NaCl solution, adding small portions at a time, and draining well between each addition. Transfer the sodium chloride extract to a Kjeldahl flask, add 25 ml. of 1 N NaOH, and distill 200 ml. into 60 ml. of standard 0.2 N H_2SO_4. Titrate the excess of acid with standard 0.1 N NaOH, using methyl red as the indicator.

NESSLERIZATION OF ADSORBED AMMONIA AFTER EXTRACTION WITH SODIUM CHLORIDE

Reagents

Nessler reagent (*9*).—In a 1-liter volumetric flask, dissolve 45.5 gm. of mercuric iodide and 35.0 gm. of potassium iodide in as little water as needed. Add 112 gm. of potassium hydroxide, mix well, cool, and dilute to 1 liter with water. Allow to settle for a few days and use the clear supernatant liquid. Store in a brown glass bottle.

Sodium tartrate, 10 percent.—Dissolve 100 gm. of $Na_2C_4H_4O_6.2H_2O$ in water and dilute to 1 liter.

Standard NH_4Cl solution and the calibration curve.—Dissolve 1.337 gm. of NH_4Cl in water and dilute to 500 ml. Preserve this solution by adding 1 ml. of chloroform. For use in the preparation of the calibration curve, dilute 5 ml. of the stock solution to 500 ml. One ml. of the diluted solution contains 0.0005 m. e. of ammonium. Measure out aliquots of this solution, containing 0 to 0.015 m. e. of ammonium, into a series of 125-ml. Erlenmeyer flasks, add 0.5 ml. of the acidified 10 percent NaCl solution, dilute with water to 45.5 ml., add 1 ml. of 10 percent sodium tartrate solution, and proceed with nesslerization as directed under the procedure below.

Procedure

After the extraction of the adsorbed ammonium with 450 ml. of 10 percent sodium chloride solution as directed in the procedure for the distillation of adsorbed ammonia, transfer the sodium chloride extract to a 500-ml. volumetric flask, make up to volume with water, and mix. Pipette a 0.5-ml. aliquot of the sodium chloride extract into a 125-ml. Erlenmeyer flask; add 45 ml. of water, 1 ml. of 10 percent sodium tartrate solution, and 2.5 ml. of Nessler reagent, mixing well after each addition. After 25 minutes measure the transmittancy of the solution at 410 mμ. Use a blue filter.

For a 50-gm. sample of soil and 0.5-ml. aliquot of the sodium chloride extract, the milliequivalents of ammonia found when multiplied by 2,000=exchange capacity, milliequivalents per 100 gm. of soil.

EXCHANGE CAPACITY BY SUMMATION OF EXCHANGEABLE CATIONS

Compute the cation exchange capacity from the sum of the exchangeable metal cations and the exchangeable hydrogen as obtained by the triethanolamine method (see p. 11). In acid soils of the humid regions the exchangeable sodium may be neglected in this computation.

COMMENTS

Pending further investigation, two alternative methods for the determination of the cation exchange capacity are proposed: (1) By summation of the exchangeable metal cations and the exchangeable hydrogen as determined by the triethanolamine method (see below); and (2) by direct determination of the adsorbed ammonium after leaching the soil with 1 N ammonium acetate solution. With certain soils these two methods will not give the same results.

The determination of the quantity of ammonium adsorbed is preceded by washing out the excess of ammonium acetate with alcohol. After washing out this excess avoid prolonged drying of the soil, as this may result in some loss of the adsorbed ammonium. The customary practice of "neutralizing" the alcohol with ammonium hydroxide, using bromthymol blue indicator or the glass electrode, is not only meaningless but is certain to lead to high results for the cation exchange capacity, for reasons pointed out by Peech (*9*). The quantity of adsorbed ammonium is determined by direct distillation in the presence of alkali or after first replacing the adsorbed ammonium with sodium chloride solution, followed by the determination of the ammonia in the extract by distillation or by direct nesslerization. Each method has certain disadvantages. With soils high in organic matter, direct distillation gives high results, owing to some decomposition of the soil organic matter. On the other hand, some losses of ammonia may be incurred from the calcareous soils during the extraction with sodium chloride solution under reduced pressure.

Determination of Exchangeable Hydrogen

EXCHANGEABLE HYDROGEN BY THE TRIETHANOLAMINE METHOD

Reagents

Buffer solution.—Barium chloride (0.5 N), triethanolamine (0.2 N). Dilute 100 ml. of commercial triethanolamine (specific gravity 1.126 about 8 N) with 1,000 ml. of water and partially neutralize with HCl to adjust to pH 8.1 to 8.2 (this requires approximately 360 ml. of 1 N HCl). Make up to 2 liters with water and mix with 2 liters of a solution containing 250 gm. of $BaCl_2.2H_2O$. Protect from CO_2 of the air.

Replacement solution.—Barium chloride. Dissolve 250 gm. of $BaCl_2.2H_2O$ in 4 liters of distilled water, add 10 ml. of buffer solution, and mix.

Standard hydrochloric acid.—0.100 N; standardize according to accepted procedures.

Procedure

Place 10 gm. of soil in a 125-ml. Erlenmeyer flask, add 25 ml. of buffer solution, and allow the flask to stand for one-half hour, mixing the contents occasionally by swirling. Transfer to a Gooch crucible containing a moist paper disk (Whatman No. 42) and filter into a 250-ml. flask. Use an additional 25 ml. of buffer solution to aid in the

transfer of all the soil to the crucible. The rate of filtration should be such that not less than 30 minutes is required to complete this filtration and leaching. Now, by adding small increments, leach the soil with 100 ml. of the replacement solution.

To the leachate add 10 drops of bromcresol green and 2 drops of methyl red. Titrate with 0.100 N HCl. The end point can be chosen as any point during the progressive color change from a bluish green through violet to pink. This end point should be checked against a blank containing 50 ml. of buffer solution and 100 ml. of replacement solution and titrated to the same end point with the 0.100 N hydrochloric acid. This end point should be reached when titrating the soil extracts. All calculations are made with this blank determination as a reference.

EXCHANGEABLE HYDROGEN BY DIFFERENCE

Subtract the sum of the exchangeable metal cations (Ca, Mg, K, Na, and Mn) from the exchange capacity as determined by the ammonium adsorption method, as given on page 9.

COMMENTS

The exchangeable sodium content of acid soils of the humid regions is usually small and may be neglected in the above computation of the quantity of exchangeable hydrogen by difference. The direct titration of exchangeable hydrogen in the ammonium acetate extracts with standard ammonium hydroxide, as employed by Schollenberger (*13*), is difficult because the ammonium acetate solution is highly buffered at pH 7. With proper precautions, however, direct titration of the ammonium acetate extract to the original pH of the ammonium acetate solution, as determined by the glass electrode, should give satisfactory and comparable results.

As already pointed out, with certain soils the quantity of exchangeable hydrogen determined by the ammonium acetate method may vary widely from that obtained by the triethanolamine method. Both methods, however, are tentatively recommended until further data are available for their comparison.

Macromethods for Determination of Exchangeable Cations

Calcium, magnesium, and manganese are determined in the same aliquot of Solution A (see p. 8). This aliquot should represent 20 gm. of soil; a larger aliquot should be taken if calcium and magnesium are suspected to be low. Ammonium acetate extracts of most soils do not contain sufficient iron and aluminum to interfere seriously in the determination of calcium and magnesium; consequently, no provision is made for their removal in the macromethods. Magnesium and manganese in this procedure are coprecipitated as the ammonium phosphates; the manganese in the precipitate is determined colorimetrically, and proper correction is then applied in computing the quantity of magnesium.

CALCIUM

Reagents

Oxalic acid; 5 percent aqueous solution.
Bromcresol green; 0.04 percent aqueous solution.
Ammonium hydroxide; 1 N.
Sulfuric acid; 1 N.
Standard potassium permanganate; 0.05 N.
Wash solution; aqueous solution saturated with calcium oxalate.

Asbestos.—Digest the asbestos in 1 N HNO_3 solution containing just sufficient potassium permanganate to give a deep purple color. Add more permanganate if the color disappears; digest for 24 hours, or until the permanganate color is permanent. Destroy the excess permanganate with oxalic acid and wash thoroughly on a Buchner funnel.

Procedure

Place 40 ml. of Solution A (see p. 8) in a 250-ml. beaker and dilute to approximately 100 ml. If calcium is suspected to be low, dilute only to 50 ml. Add 5 ml. of oxalic acid, heat the contents of the beaker almost to boiling, and add 1 ml. of bromcresol green. Adjust approximately the pH of the hot solution to 4.6 by adding N ammonium hydroxide slowly with constant stirring. Digest the contents of the beaker at about 80° C. for 1 hour, or until the supernatant liquid is clear. Collect the calcium oxalate precipitate on a compact asbestos pad in a Gooch crucible. Rinse the beaker four times with water saturated with calcium oxalate, pouring the washings into the crucible. Wash the precipitate five more times with water saturated with calcium oxalate.

Remove the Gooch crucible from its holder, rinse off the outside, remove the pad, and place both pad and crucible in the original beaker. Add 100 ml. of hot (90° C.) normal sulfuric acid, stir until the calcium oxalate is dissolved, and titrate with standard potassium permanganate solution.

MAGNESIUM

Reagents

Nitric acid; specific gravity 1.42.
Ammonium hydroxide; specific gravity 0.90.
Hydrochloric acid; 6 N.
Diammonium-hydrogen phosphate; 10 percent aqueous solution.
Standard sulfuric acid; 0.1 N.
Standard sodium hydroxide; 0.1 N.
Bromcresol green; 0.04 percent aqueous solution.

Procedure

Transfer the filtrate from the calcium determination to a 150-ml. beaker, add 20 ml. of nitric acid, and evaporate to dryness, taking due precautions against spattering. Dissolve the residue in 5 ml. of 6 N HCl solution and transfer to a 200-ml. Erlenmeyer flask. Dilute to about 75 ml., just neutralize with NH_4OH, and add 5 ml. of diammonium-hydrogen phosphate solution followed by 10 ml. of concen-

trated NH_4OH (specific gravity 0.90). Stir the solution vigorously until the precipitate forms and let stand overnight. Filter on a 9-cm. Whatman No. 40 filter. Rinse the flask five times with 1 N NH_4OH, pouring the washings into the filter. Wash the precipitate in the filter five more times with 1 N NH_4OH.

Place the wet filter containing the magnesium and manganese ammonium phosphate precipitate on a watch glass and allow to dry (not above 40° C.) until free of ammonia. Place the dry filter in the original flask; add 10 ml. of standard sulfuric acid (or more if necessary to dissolve the precipitate) and 1 ml. of bromcresol green indicator. After the precipitate has dissolved, add 50 ml. of water, stopper the flask, and shake vigorously until the filter paper is macerated. Remove the stopper and rinse it, as well as the walls of the flask, with water. Titrate with standard sodium hydroxide to a greenish-blue color. The correct end point is best ascertained by comparison with a color of a standard, prepared by placing 0.1 gm. of potassium dihydrogen phosphate, 70 ml. of water, and 1 ml. of bromcresol green in a 200-ml. Erlenmeyer flask.

MANGANESE

Reagents

Sulfuric acid; 0.1 N.
Phosphoric acid; 85 percent.
Hydrogen peroxide; 10 percent.
Sodium metaperiodate.

Procedure

Filter the solution remaining from the titration of magnesium and manganese phosphates into a 150-ml. beaker and wash the filter with 0.1 normal sulfuric acid. Evaporate the filtrate nearly to dryness, rinse the beaker with a little water, add 2 ml. of hydrogen peroxide, and evaporate to dryness to destroy any organic matter and to expel the excess of hydrogen peroxide. Dissolve the residue in 35 ml. of water and add 5 ml. of 85 percent phosphoric acid solution. Add about 0.3 gram of sodium periodate. Bring the solution cautiously to a boil and continue boiling until the color development is complete. Full color develops usually within 20 minutes. When the solution is cool, transfer it to a volumetric flask (50 or 100 ml., depending upon the quantity of manganese present) and dilute to volume with 5 percent phosphoric acid solution that has been boiled with a little sodium periodate. Mix well and measure the transmittancy at 530 mμ. (Use a green filter.) The quantity of manganese is obtained from a calibration curve prepared according to the directions given on page 21.

To correct for manganese in the magnesium precipitate, convert the manganese to an equivalent volume of standard sulfuric acid and subtract this from the titration value.

1 mg. Mn=0.364 ml. 0.1 N H_2SO_4
1 ml. 0.1 N H_2SO_4=1.216 mg. Mg

POTASSIUM

Reagents

Trisodium cobaltinitrite solution.—Prepare an aqueous solution containing 1 gm. of the C. P. salt in each 5-ml. solution. Filter before use. The solution is stable for a few days if kept in the refrigerator, but it is preferable to make up a fresh supply for each set of determinations.

Nitric acid; 1 N and 0.01 N.

Procedure

Place an aliquot of Solution A equivalent to 20 gm. of soil in a 50-ml. beaker and evaporate to dryness. Dissolve the residue in 1 ml. of 1 N HNO_3 and then add 10 ml. of water. This solution must not contain any suspended material. Add 5 ml. of the sodium cobaltinitrite solution, mix, and allow to stand for 2 hours at 20° ±2° C. Filter through asbestos in a Gooch crucible, the tare of which is known. Use 0.01 N HNO_3 in the wash bottle to make the transfer and wash the precipitate in the crucible eight times with 2-ml. portions of 0.01 N HNO_3. Finally wash the crucible and the precipitate five times with 2-ml. portions of 95 percent alcohol. Remove the crucible, wipe the outside with a cloth, dry for 1 hour at 110° C., cool in a desiccator, and weigh. The composition of the precipitate is given by the formula $K_2NaCo(NO_2)_6.H_2O$; K=17.22 percent.

As an alternative method potassium may be determined volumetrically. Omit the five alcohol washings in the gravimetric method and proceed as follows: Introduce the proper measured quantity of 0.05 normal potassium permanganate in a 400-ml. beaker, dilute with water to about 150 ml., and add 5 ml. of concentrated sulfuric acid. Add the crucible and the precipitate to the acidified permanganate, stir to keep the precipitate beneath the surface of the liquid, and heat. If the color seems likely to disappear, remove the beaker from the flame and add an additional measured supply of standard permanganate. Heat to nearly boiling, remove from the flame, add a small excess of standard oxalic acid, and titrate the excess oxalic acid with standard permanganate. The difference between the quantities of permanganate and oxalic acid used corresponds to the quantity of permanganate reduced by the cobaltinitrite precipitate.

Net milliliters of $KMnO_4$ × normality of $KMnO_4$ × 7.108 = milligrams of K in the sample taken.

Comments

The above method is essentially that described by Wilcox (*16*). The time and temperature of the precipitation are critical, and any radical departure from those given may introduce serious errors. Standard potassium solutions should be checked frequently, and if necessary the results should be calculated, using the empirical factor found. It has been observed that sodium cobaltinitrite purchased from different sources may give different recoveries of potassium from a standard potassium solution if the theoretical factor given above is used for calculation of the results.

SODIUM [3]

Reagents

Uranyl magnesium acetate reagent.—Dissolve 32 gm. of uranyl acetate [$UO_2(C_2H_3O_2)_2.2H_2O$] and 100 gm. of magnesium acetate [$Mg(C_2H_3O_2)_2.4H_2O$] in about 200 ml. of water; warm if necessary. Cool, add 20 ml. of 99.5 percent acetic acid and 475 ml. of 95 percent ethyl alcohol; dilute to 1 liter and mix well. Allow the solution to stand in a dark place for 48 hours and filter into a Pyrex bottle. Store the filtered solution in a dark place.

Alcohol saturated with sodium uranyl magnesium acetate.—Shake up some 95 percent alcohol with a few grams of precipitated sodium uranyl magnesium acetate in a stoppered Pyrex bottle and leave for 24 hours. Filter the almost clear supernatant liquid through a Whatman No. 44 filter and store in a second bottle with a further supply of crystalline salt. This gives a stock supply of alcohol saturated with the sodium salt, and after filtration it is always ready for use as the washing solution. Always add fresh additions of alcohol to the first bottle and leave for 24 hours or longer before transferring to the second bottle, for reasons given by Piper (*11*).

Procedure

Place an aliquot of Solution A, representing 5 to 10 gm. of soil, in a 50-ml. Pyrex beaker and evaporate to dryness. Dissolve the residue in 6 ml. of water. It is not necessary to filter this solution if there is a slight turbidity. Add 15 ml. of uranyl magnesium acetate reagent and stir for 15 seconds or until a precipitate forms. Cover the beaker and allow to stand for 1 hour, but not longer than 2 hours.

Filter through a small Gooch charged with asbestos. Wash the precipitate with 2 ml. of uranyl magnesium acetate reagent and then five times with 95 percent alcohol saturated with the triple salt, transferring the precipitate quantitatively to the Gooch crucible. Dry in an oven at 105° C. for 1 hour, then cool the crucible in a desiccator, and weigh as $Na(UO_2)_3.Mg(CH_3COO)_9.8H_2O$. After weighing, wash the crucible with several portions of hot water, dry again, and weigh. This second weight gives the weight of the crucible plus uranyl phosphate and any insoluble residue that was not removed before the precipitation; the difference in weight corresponds to the sodium uranyl magnesium acetate. Carry out a blank determination on all reagents used.

Micromethods for Determination of Exchangeable Cations [4]

APPARATUS

Electric muffle with a rheostat and a pyrometer.

A centrifuge that will accommodate 24 15-ml. centrifuge tubes. International Equipment Company laboratory centrifuge size 1 or 2, Type SB, centrifuging at 2,000 r. p. m., has been successfully employed in centrifuging all precipitates. Higher speeds are likely to lead to breakage of centrifuge tubes.

[3] For further discussion of this method, see Piper (*11*).

[4] For further discussion of the following micromethods see the original publications by Peech (*8, 9*).

A spectrophotometer or a photoelectric colorimeter provided with light filters and optical cells 1.0 cm. in thickness. The following Corning heat-resisting glass color filters are satisfactory: Light red No. 2418 for magnesium determination; emerald green No. 4084 for potassium and manganese determinations; lantern blue No. 5543 for sodium and ammonium determinations.

Pyrex 15-ml. conical centrifuge tubes, graduated to contain 13 ml. (by circling with a diamond point), and numbered permanently. Another set of tubes, also graduated at 13 ml., somewhat more constricted at the tip, so that the outside diameter measured 10 mm. from the tip is less than 8 mm., are preferable for use in the determination of magnesium.

Pyrex tubes, 125 by 15 mm., graduated at 11 ml.

A water bath with a removable rack to hold 48 centrifuge tubes is very useful and can be made of sheet copper.[5] The removable rack permits cooling the tubes conveniently by immersion in a similar container filled with cold water. If the rack is properly constructed the contents of the tube can be mixed without the use of a stirring rod by simply spinning the tube in the bath and allowing the solution to whirl inside the tube.

Another bath, consisting of a 1-liter beaker fitted with a round sheet-copper lid that supports a centrifuge-tube holder and a thermometer, is used in the permanganate titration of calcium. The titration can be thus performed at constant temperature and the end point observed without removing the tube from the bath.

A motor stirrer may be used to advantage for stirring the solutions in the centrifuge tubes during precipitations and, when washing, for breaking up precipitates packed by centrifuging. In addition to the motor stirrer, stirring rods made of 3-mm. glass rod, with one end flattened to form a disk 9 mm. in diameter, are useful for stirring the solutions by hand.

0.5-ml., 1-ml., 2-ml., 3-ml., and 10-ml. transfer pipettes.

SEPARATION OF MANGANESE, IRON, ALUMINUM, AND PHOSPHATE PRIOR TO THE DETERMINATION OF CALCIUM AND MAGNESIUM

Reagents

Ammonium chloride, 25 percent.—Dissolve 250 gm. of ammonium chloride in water and dilute to 1 liter.

Ammonium hydroxide, 0.60 N.

Bromine water; saturated solution of bromine in water.

Sodium acetate, 10 percent.—Dissolve 100 gm. of sodium acetate ($NaC_2H_3O_2 .3H_2O$) in water and dilute to 1 liter.

Methyl red, 0.02 percent.—Triturate 0.04 gm. of methyl red with 1.5 ml. of 0.1 N NaOH and dilute to 200 ml. with water.

Procedure

Transfer a 2-ml. aliquot of Solution A (see p. 8) to a 15-ml. centrifuge tube, add 3 ml. of water and 2 ml. of 10 percent sodium acetate solution, and mix the contents; then add 1 ml. of 0.1 N sodium hydroxide and mix again. Place the centrifuge tube in a water bath at 95° C., add 1 ml. of bromine water, and mix by spinning the tube

[5] See Peech (8) for details of construction.

in the bath and allowing the solution to whirl inside the tube. Maintain this temperature for at least 1 hour to flocculate manganese dioxide and to expel the excess of bromine. Then add 2 ml. of 25 percent ammonium chloride solution and digest for about 15 minutes longer. Add 1 drop of methyl red, and if the color of the indicator persists, indicating complete expulsion of bromine, remove the tube from the water bath, cool, add 0.6 N ammonium hydroxide from a burette until the color of the solution changes to yellow, and then add 2 drops in excess. A rather constant quantity, 0.5 ml., of ammonium hydroxide solution is usually required and may be added at one time. Make up to a volume of 13 ml. with water, add 5 drops in excess to allow for evaporation, mix the contents with a stirring rod, and digest in a water bath at 80° C. for 5 minutes to flocculate the precipitate. Centrifuge while hot for 10 minutes at 2,000 r. p. m. Designate the supernatant liquid as *Solution B*.

Comments

In the precipitation of manganese by bromine the addition of 2 ml. of 10 percent sodium acetate solution and 1 ml. of 0.1 N sodium hydroxide to the 2-ml. aliquot will buffer the solution at pH 5.7, which is sufficiently high to prevent dissolution of the manganese dioxide. When dealing with soils high in calcium, an aliquot of only 1 ml. of Solution A is taken and the addition of 1 ml. of 0.1 N sodium hydroxide is then omitted. Both ammonium chloride and ammonium hydroxide are added after the excess of bromine has been expelled to preclude oxidation of the ammonium salts and consequent increase in the acidity of the solution. Further digestion in the presence of ammonium chloride assures the removal of the last trace of bromine, which would otherwise destroy the indicator used later. The pH of Solution B is usually about 6.8.

CALCIUM

Reagents

Saturated calcium oxalate.—Saturate water with calcium oxalate, allow the excess precipitate to settle out, and siphon the clear solution before use.

Ammonium oxalate, 3 percent.—Dissolve 30 gm. of ammonium oxalate [$(NH_4)_2C_2O_4.H_2O$] in water and dilute to 1 liter.

Hydrochloric acid, 0.5 N.

Sulfuric acid, 10 percent.

Standard potassium permanganate, 0.025 N and 0.05 N.—Dilute 0.1 N stock solution and standardize against sodium oxalate. The 0.025 N standard permanganate solution is used when the quantity of calcium oxalate precipitate is small.

Procedure

Pipette a 10-ml. aliquot of Solution B into a 15-ml. centrifuge tube without disturbing the precipitate of manganese, iron, and aluminum. This is best done by holding the tube in front of a mirror while pipetting. Add 0.5 ml. of 0.5 N hydrochloric acid and 1 ml. of water. Place the tube in a water bath at 70° C., mix the contents by spinning the tube, add 2 ml. of 3 percent ammonium oxalate, and mix thoroughly again. Digest for 30 minutes at 70° C. Remove the tube from the bath and let stand for 30 minutes.

Make to a volume of 13 ml. and mix thoroughly. It is seldom necessary to adjust the volume, since 0.5 ml. is provided in excess to compensate for evaporation during digestion. Centrifuge for 15 minutes at 2,000 r. p. m., decant the clear supernatant liquid into a dry test tube, and save for the determination of magnesium. Designate this as *Solution C*.

Allow the centrifuge tube, inverted at about a 45° angle, to drain for several minutes on filter paper, add 5 ml. of saturated aqueous solution of calcium oxalate, break up the precipitate with a stirring rod, wash the rod, and centrifuge for 15 minutes. Decant, discarding the clear solution, and drain the tube for several minutes. Add 5 ml. of 10 percent sulfuric acid solution, heat to 70° C. in a water bath, and titrate with standard permanganate. If the titer is greater than 5 ml., add about 4 drops of concentrated sulfuric acid before completing the titration.

For a 50-gm. sample of soil and 2-ml. of Solution A, 1 ml. of 0.05 N permanganate=1.62 m. e. per 100 gm., or 650 pounds of calcium per 2,000,000 pounds of soil.

Comments

In order to prevent coprecipitation of magnesium, calcium is precipitated at pH 5. One washing of calcium oxalate precipitate is sufficient if the centrifuge tube has been drained properly each time after decantation.

MAGNESIUM

Reagents

Ammonium hydroxide.—Concentrated, specific gravity 0.90.

Hydrochloric acid, 0.5 N.

Ammoniacal ammonium acetate wash solution.—To 400 ml. of 1 N ammonium acetate solution add 200 ml. of distilled water and 16 ml. of concentrated ammonium hydroxide.

8-hydroxyquinoline, 2 percent.—Prepare a fresh supply of this reagent as needed by dissolving 0.5 gm. of 8-hydroxyquinoline in 25 ml. of 95 percent ethyl alcohol.

Phenol reagent.—To 750 ml. of water in a 2-liter flask add 100 gm. of sodium tungstate ($Na_2WO_4.2H_2O$), 20 gm. of phosphomolybdic acid ($20MoO_32H_3PO_4.48H_2O$), and 50 ml. of 85 percent phosphoric acid. Boil gently for 2 hours, cool, and dilute to 1 liter with water. The phosphomolybdic acid specified is supplied by Merck & Co. The use of a reagent prepared from phosphomolybdic acid of indefinite composition, particularly with respect to water of crystallization, is likely to lead to troublesome turbidities during color development.

Sodium carbonate, 20 percent.—Dissolve 200 gm. of the anhydrous salt in water, dilute to 1 liter, and filter if necessary.

Standard magnesium quinolate solution and calibration curve.—Dissolve 0.15 gm. of magnesium sulfate ($MgSO_4.7H_2O$) in 100 ml. of 10 percent ammonium chloride solution, heat to 60° to 70° C., add 10 ml. of the 8-hydroxyquinoline reagent, and render the solution alkaline with 4 ml. of concentrated ammonium hydroxide. Digest for 10 minutes at 60° to 70°, collect the precipitate on a fritted-glass crucible, wash with hot dilute ammonium hydroxide (0.4 N), and dry at 140°. Dissolve 0.0643 gm. of the dried precipitate in 20 ml.

of 0.5 N hydrochloric acid and dilute to 500 ml. with water. One ml. contains 0.01 mg. of magnesium. Introduce aliquots of this solution, containing 0.0025 to 0.06 mg. of magnesium, into a series of 50-ml. volumetric flasks, dilute with water to 35 ml., and proceed with color development as directed in the procedure for magnesium. Plot the transmittancies of the standard solutions against milligrams of magnesium taken for color development on a semilogarithmic graph paper.

Procedure

Introduce a 10-ml. aliquot of the solution from the calcium determination (Solution C) into a 15-ml. centrifuge tube. Place the tube in a bath at 70° C., add 0.8 ml. of 2 percent alcoholic solution of 8-hydroxyquinoline, mix immediately by stirring, and then add 0.4 ml. of concentrated ammonium hydroxide from a burette. Stir vigorously for 1 minute, or longer if the quantity of magnesium is extremely small, until full turbidity develops. Wash the stirring rod with a few drops of water and replace the centrifuge tube in a water bath at 70° C. for 10 minutes.

After digesting for 10 minutes, cool to about 25° C., and allow to stand for 45 minutes to assure complete precipitation of magnesium. (If the solution is not yellow, which is very seldom the case, the quantity of the 8-hydroxyquinoline reagent added was insufficient to precipitate all the magnesium.) Wash down the precipitate by adding slowly 0.5 ml. of 95 percent alcohol down the sides of the tube so as to form a layer of alcohol on top of the solution and thus prevent creeping of the precipitate. Centrifuge for 15 minutes at 2,000 r. p. m., and by using suction draw off 2 to 3 ml. of the clear liquid from the top to remove the layer of alcohol.

Decant carefully, discarding the solution, and wipe the mouth of the tube with filter paper. Add 5 ml. of ammoniacal ammonium acetate, wash solution down the sides of the tube, break up the precipitate with a stirring rod, and wash off the rod into the tube. Add 0.5 ml. of alcohol slowly down the sides of the tube to prevent creeping of the precipitate and centrifuge for 15 minutes. Draw off the layer of alcohol, decant, and repeat the washing once more as directed above. Dissolve the precipitate in 4 ml. of 0.5 N hydrochloric acid, dilute to 13 ml. with water, stopper, and mix.

Transfer a 2-ml. aliquot (use 1 ml. if the solution is distinctly yellow) to a 50-ml. volumetric flask and add 35 ml. of water, 5 ml. of 20 percent sodium carbonate solution, and 3 ml. of phenol reagent, mixing the contents well after each addition. Place the flask in boiling water for 1 minute, remove from the bath, and allow to stand for 15 minutes. Then cool, make to volume, mix, and measure the transmittancy at 625 mμ.

For a 50-gm. sample of soil and 2-ml. aliquot of Solution A, 1 mg. of magnesium precipitated=3.48 m. e. per 100 gm., or 845 pounds of magnesium per 2,000,000 pounds of soil.

Comments

The conditions for precipitation of magnesium outlined in the procedure have given consistently good results and should be followed closely. Although the presence of oxalate seems to inhibit complete precipitation of magnesium if the solution is not stirred sufficiently, excellent recoveries even of small quantities of magnesium have been

obtained from solutions containing large quantities of ammonium oxalate, provided the solution is stirred vigorously for about 1 minute after the addition of the reagents. Because the precipitate is light and does not pack well upon centrifuging, considerable care must be exercised in decanting the supernatant liquid in order to prevent loss of the precipitate. For this purpose, it is advisable to select centrifuge tubes that are somewhat more constricted at the tip. The precipitate shows much less tendency to break away from the bottom of the tube and proper drainage of the tubes is facilitated if the layer of alcohol is drawn off before decanting the supernatant liquid.

MANGANESE

Reagents

Sodium periodate.—The more soluble sodium metaperiodate is preferred to the potassium salt commonly recommended.

Phosphoric acid, 85 percent.

Standard manganese solution and calibration curve.—To 22.8 ml. of 0.1 N standard potassium permanganate in a 250-ml. Erlenmeyer flask add about 50 ml. of water and 1.0 ml. of concentrated sulfuric acid. Heat to boiling and reduce the permanganate by the addition of sodium sulfite, avoiding large excess. Boil off the excess sulfur dioxide and dilute to 1 liter. One ml. of this solution contains 0.025 mg. of manganese. Prepare a series of standards containing 0.005 to 0.25 mg. of manganese in 11-ml. graduated test tubes, add 1 ml. of 85 percent phosphoric acid, and proceed as directed under the determination of manganese. From the light transmission measurements, plot a calibration curve on semilogarithmic graph paper.

Procedure

Transfer a 1- to 3-ml. aliquot of Solution A, depending upon the quantity of manganese, to a test tube graduated at 11 ml. (The quantity of manganese present may be estimated roughly from the previous separation of manganese in the determination of calcium and magnesium.) Add 1 ml. of 85 percent phosphoric acid, dilute to volume with water, adding 0.3 ml. in excess to allow for evaporation, and mix with a glass stirring rod. Place in a water bath at 95° C., add about 50 mg. of sodium periodate, mix thoroughly again with a glass rod, and leave in the bath for 1 hour to assure full development of the color. Cool, make to volume if necessary, mix, and measure the transmittancy at 530 mμ.

For a 50-gm. sample of soil and 3-ml. aliquot of Solution A, 1 mg. of manganese found =0.607 m. e. per 100 gm., or 333 pounds per 2,000,000 pounds of soil.

Comments

The use of phosphoric acid instead of the sulfuric acid, often employed in the oxidation of manganese by periodate, offers several advantages. The oxidation of manganese, regardless of the quantity present, proceeds very rapidly in phosphoric acid solution over a wide range in acidity without the occasional formation of off-color tints due to precipitation of manganese.

Precipitation of calcium sulfate is also obviated. The practice of adding persulfate to destroy traces of organic matter, even a few min-

utes prior to the addition of periodate, is certain to cause precipitation of manganese, especially at higher concentrations, and should be avoided. The small quantity of organic matter that may be present at this stage, owing to incomplete ashing, has not been found to cause serious trouble. Inasmuch as an excess of periodate is added, the small quantity of chloride present does not interfere and need not be removed.

POTASSIUM

Reagents

Ethyl alcohol, 70 percent.—Dilute 500 ml. of 95 percent ethyl alcohol with 180 ml. of water.

Nitroso-R salt, 0.5 percent.—Dissolve 0.5 gm. of nitroso-R salt (disodium salt of 1-nitroso-2-hydroxy 3,6-naphthalene disulfonic acid) in 100 ml. of water. When not exposed to light the reagent is stable for several weeks.

Sodium cobaltinitrite, 25 percent.—Dissolve 25 gm. of potassium-free trisodium cobaltinitrite in water, dilute to 100 ml., and filter. Store in a refrigerator when not in use. Prepare a sufficient quantity every 3 days, or preferably as needed.

Sodium pyrophosphate, 5 percent.—Dissolve 5 gm. of powdered sodium pyrophosphate ($Na_4P_2O_7.10H_2O$) in water and dilute to 100 ml.

Sodium acetate, 2.5 N.

Sulfuric acid, 2.0 N.

Standard potassium solution and calibration curve.—Dissolve 0.9533 gm. of dried potassium chloride in water and dilute to 500 ml. One ml. contains 1 mg. of potassium. Dilute a portion of this stock solution to contain 0.5 mg. of potassium per milliliter. Measure out aliquots of the standard solutions, containing from 0.1 to 2.0 mg. of potassium, into a series of 15-ml. centrifuge tubes, add 0.3 ml. of 1 N nitric acid, and dilute to 3 ml. with distilled water. Mix, and carry these standards through the procedure outlined for potassium. From the resultant data construct a calibration curve by plotting on semilogarithmic graph paper the transmittancies against milligrams of potassium precipitated.

Procedure

Introduce a 3-ml. aliquot of Solution A into a 15-ml. centrifuge tube. If more than 2 mg. of potassium is suspected in the 3-ml. aliquot, use a smaller aliquot and dilute to 3 ml. with 0.1 N nitric acid. Add 1 ml. of sodium cobaltinitrite reagent and mix the contents thoroughly by swirling the tube. Stopper, and let stand in the refrigerator (10° C.) for 1 hour, then add 4 ml. of 70 percent alcohol, mix thoroughly with a stirring rod, wash the rod with 70 percent alcohol, and centrifuge for 15 minutes at 2,000 r. p. m. Decant the supernatant liquid, drain the tube for several minutes by inverting at about a 45° angle, add 5 ml. of 70 percent alcohol down the walls of the tube, break up the precipitate with a stirring rod, wash the rod with alcohol, and centrifuge for 10 minutes. Decant the clear solution, allow the tube to drain for several minutes, wipe the mouth of the tube with filter paper, and repeat the washing with 5 ml. of 70 percent alcohol. Add 5 ml. of 2 N sulfuric acid, place the tube in a water bath at 70° C., and mix the contents occasionally by spinning the tube until the precipitate is completely dissolved; then add 5 to 7 ml. of water and heat

for several minutes more to dissolve any precipitate adhering to the sides of the tube. Cool, dilute to 13 ml., stopper, and mix thoroughly.

Introduce a 1-ml. aliquot of the solution into a 25-ml. volumetric flask; add 15 ml. of water, 1 ml. of 5 percent sodium pyrophosphate solution, 1 ml. of 2.5 N sodium acetate solution, and 2 ml. of 0.5 percent solution of nitroso-R salt, mixing well after each addition. Dilute to 25 ml., mix well, and after 20 minutes measure the transmittancy of the solution at 530 mμ.

For a 50-gm. sample of soil and 3-ml. aliquot of Solution A, 1 mg. of potassium found precipitated = 0.426 milliequivalent per 100 gm., or 333 pounds of potassium per 2,000,000 pounds of soil.

Comments

In developing the cobalt color with nitroso-R salt, it is important to control the pH of the solution. The color fails to develop below pH 3, but develops slowly between pH 3 and 4. Between pH 4 and 5 it develops rapidly, and the intensity is practically constant; above pH 5 the intensity increases gradually with increase in pH. The addition of 1 ml. of 5 percent solution of sodium pyrophosphate and 1 ml. of 2.5 N sodium acetate solution to the 1-ml. aliquot of the solution of the cobaltinitrite precipitate will buffer the final solution strongly at pH 5. Sodium pyrophosphate was found effective in preventing the interference from small quantities of iron that might precipitate as the phosphate together with the potassium cobaltinitrite, and that would react subsequently with the nitroso-R salt to impart a greenish cast to the final color developed.

SODIUM

Reagents

Uranyl magnesium acetate reagent.—Dissolve 32 gm. of uranyl acetate [$UO_2(C_2H_3O_2)_2.2H_2O$] and 100 gm. of magnesium acetate [$Mg(C_2H_3O_2)_2.4H_2O$] in water by warming. Cool, add 20 ml. of 99.5 percent acetic acid and 475 ml. of 95 percent ethyl alcohol; dilute with water to 1 liter and mix well. Filter after 2 days and store in a Pyrex bottle. The reagent is stable if kept in the dark.

Ethyl acetate-acetic acid wash solution.—Dilute 300 ml. of ethyl acetate to 1 liter with 99.5 percent acetic acid.

Ethyl ether; c. p. anhydrous.

Sulfosalicylic acid, 0.35 N.—Dissolve 12.5 gm. of sulfosalicylic acid in water and dilute to 250 ml. Titrate a 5-ml. aliquot with 0.1 N sodium hydroxide, using phenolphthalein as an indicator, and adjust exactly to 0.35 N.

Sodium acetate, 10 percent.—Dissolve 50 gm. of sodium acetate ($NaC_2H_3O_2.3H_2O$) in water and dilute to 500 ml.

Standard sodium solution and calibration curve.—Dissolve 1.525 gm. of dried sodium chloride in water and dilute to 1 liter. One ml. contains 0.60 mg. of sodium. Measure out aliquots of this solution to give 0.06 to 1 mg. of sodium into a series of 15-ml. centrifuge tubes. Add 0.2 ml. of 1 N nitric acid, dilute with water to 2 ml., and mix the contents. Carry these standard solutions through the procedure outlined for the determination of sodium and plot on semilogarithmic graph paper the transmittancies against the respective quantities of sodium taken for precipitation.

Procedure

Pipette a 2-ml. aliquot of Solution A, containing 0.06 to 1 mg. of sodium, into a 15-ml. centrifuge tube. Add 5 ml. of uranyl magnesium acetate reagent and stir vigorously for 1 minute. Rinse the stirring rod with 0.5 ml. of the reagent, mix by swirling the tube, and allow to stand in a water bath at 15° C. for 1½ hours. Centrifuge for 15 minutes at 2,000 r. p. m., decant, drain for several minutes, and wipe the mouth of the tube with filter paper. Add 4 ml. of ethyl acetate-acetic acid, wash solution down the sides of the tube, break up the precipitate with a stirring rod, rinse the rod with about 0.5 ml. of the wash solution, and centrifuge for 10 minutes. Decant and drain; wipe the mouth of the tube with filter paper. Add 4 ml. of diethyl ether down the sides of the tube, break up the precipitate with a stirring rod, wash the rod with about 1 ml. of ether, and centrifuge for 8 minutes. Decant and drain for not more than 1 minute, as longer draining may cause dropping of the dry precipitate from the tube. Repeat the washing with 4 ml. of ether as before. Put the tube in a warm place to evaporate the last traces of ether.

Dissolve the precipitate in water, dilute to 13 ml., stopper, and mix well by inversion. Centrifuge for 10 minutes to remove the trace of insoluble uranyl phosphate that may be present. Introduce a 5-ml. aliquot of the solution containing sodium uranyl magnesium acetate into a dry 25-ml. Erlenmeyer flask; add 5 ml. of water and 1 ml. of 0.35 N sulfosalicylic acid solution and mix; then add 1 ml. of 10 percent sodium acetate solution and mix well. After 15 minutes, measure the transmittancy at 450 mμ.

For a 50-gm. sample of soil and 2-ml. aliquot of Solution A, 1 mg. of sodium found precipitated=1.09 m. e. per 100 gm., or 500 pounds per 2,000,000 pounds of soil.

Comments

The smallest quantity of sodium that can be precipitated completely under conditions outlined in the procedure is 0.06 mg.; with such small quantities of sodium, however, the quantity of potassium present should not exceed 2 mg. If less than 0.06 mg. of sodium is suspected to be present in the 2-ml. aliquot, Solution A should be concentrated by evaporation. As little as 0.02 mg. of sodium may be precipitated completely if the temperature during precipitation is lowered to 5° C., but unfortunately the reagent also becomes more sensitive to potassium at this temperature, resulting in poor separation of sodium even in the presence of less than 2 mg. of potassium. For this reason, the temperature and time of precipitation specified in the procedure should be observed closely.

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